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AN ELECTRON AND X-RAY DIFFRACTION INVESTIGATION OF SURFACE CHANGES ON NITRIDED-STEEL PISTON RINGS DURING ENGINE OPERATION IN NITRIDED-STEEL CYLINDER BARRELS

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SUMMARY

New and used nitrided-steel piston rings were examined by electron and X-ray diffraction in a study of the surface changes produced during engine operation. Both new and used rings, examined after degreasing, gave an electron-diffraction pattern consisting of diffuse bands; those from the used rings fell at the usual positions of the bands from polished metal surfaces. After the surface had been disturbed (acid etch, abrasion, etc.), the new ring gave the pattern of α-iron due to dilute solid solutions of the alloying elements, including nitrogen, in α-iron together with small amounts of Fe_3O_4 or γ-Fe_2O_3. The used ring in some cases gave the same pattern in addition to faint lines of γ-iron; the presence of a layer of γ-iron just under the surface is corroborated by the X-ray examination. In other cases, the used ring showed a different pattern, which was presumably that of the coating previously observed but it has not been identified. The occurrence of different patterns was due to the discontinuous character of the coating.

INTRODUCTION

Engine tests have been made using nitrided-steel piston rings with nitrided-steel cylinder barrels in an effort to increase the life of piston rings and cylinder barrels in aircraft engines. It was observed that a coating was formed on the running faces of these rings during engine operation (reference 1). This coating was thin (maximum thickness, approximately 0.0001 in.), of a highly metallic luster, corrosion-resistant, very hard, and was believed to be beneficial to the operation of the rings.

During the summer and fall of 1944, an investigation of this coating and of other possible surface changes caused by engine operation has been carried on at the NACA Cleveland laboratory. The results reported herein are concerned with finding what surface changes occur. The ultimate view in this work is that of synthesizing the beneficial coating on aircraft-engine piston rings and other sliding surfaces. The artificial production of such a coating outside of the engine should materially reduce the break-in period and increase the period between overhauls of the engine insofar as the behavior of the piston rings is the controlling factor in engine life.

The study of the surface changes occurring on piston rings requires a method that is sensitive to very thin layers. The electron-diffraction method was used by reflection from the ring faces because of the low penetration (not more than approximately 0.000001 in.) by an electron beam. Deeper surface changes in the piston rings were investigated by X-ray diffraction.

Acknowledgement is made to the Bell Telephone Laboratories, Inc., Murray Hill, N. J., for the use of their ruling machine and to the Cleveland Graphite Bronze Company for the use of their Bierbaum microhardness (scratch) tester.

APPARATUS

Electron-diffraction patterns were obtained using the diffraction unit on an RCA electron microscope. Adapters for the specimen holder were constructed at the NACA Cleveland laboratory as needed. The instrument was operated at approximately 60 kilovolts with a resulting wave length of about 0.05 A. The specimen-to-plate distance was 310 millimeters.

X-ray photographs were made with a General Electric X-ray diffraction unit using a molybdenum target and a zirconium-oxide filter to reduce the Mo K_β radiation.

A diamond-point ruling machine was used at the Bell Telephone Laboratories to plough up microscopic furrows, spaced 8000 to the inch, on segments of nitrided-steel piston rings for electron-diffraction studies. The depth of these furrows did not exceed about 0.0001 inch.

A Bierbaum microhardness (scratch) tester was used for comparative hardness tests on coated and uncoated areas on a used ring.

TEST PROCEDURE

The first ring specimens to be examined in the electron-diffraction camera were treated only for the removal of any oil film with benzene. The failure of these pieces to give sharp electron-diffraction patterns made necessary a number of roughening treatments on the ring surfaces prior to photographing the diffraction patterns. The following treatments were used separately and in various combinations: abrasion with emery, scratching with a steel file, ruling with the diamond-point machine, and etching with 2 percent nital.

Calibration of the electron-diffraction apparatus was made with the pattern of zinc oxide (fig. 1). Daily calibrations were made to check the possibility of occasional fluctuations in the operating conditions of the instrument. The following equation relating the radius of a given diffraction ring to the corresponding interplanar (Bragg) spacing is correct for the small angles involved (less than 5^o):

$$d = \frac{k}{r}$$

where

k constant (ranging from 13.8 to 14.2)

r radius of observed diffraction rings, millimeters

d interplanar (Bragg) spacing, angstrom units (10^{-8} cm)

X-ray-diffraction photographs were taken of the faces of a new and a used ring to detect subsurface changes due to engine operation. The rays were beamed upon the ring at a grazing angle with the result that penetration into the metal was of the order of 0.005 inch maximum.

RESULTS AND DISCUSSION

New and Used Piston Rings - Untreated Surfaces

The electron-diffraction examination of segments of new and used rings made after the removal of any grease layers by washing with benzene, but without any further treatment, did not show the sharp-line patterns usually required for identification purposes.

These patterns consisted of diffuse rings on a heavy background. Two diffuse diffraction rings in the patterns from new piston rings (fig. 2) gave d values of 2.03 A and 1.17 A. These rings corresponded to the first and third diffraction rings of α-iron (table I) but the other rings in the α-iron pattern did not appear. The used rings also showed patterns consisting of two diffuse bands but now at d values of 2.35 A and 1.28 A. The spacings obtained for the diffraction pattern of the used rings agreed very closely with electron-diffraction patterns from polish layers of a number of metals as given in reference 2.

The nonappearance of sharp diffraction rings in the electron-diffraction patterns from polished materials has been a subject of controversy. One theory maintains that there exists a polish layer consisting of randomly arranged atoms, as in a liquid; the second theory holds that the upper surface, although crystalline, is very smooth on a microscopic scale and consequently little transmission of electrons through projections in the surface profile can occur. In any case, the appearance of definite diffraction bands shows that a similarity exists between the uppermost stratum of material on the running face of a used piston ring and polish layers as obtained by metallographic polish. The polish layer has been called the Beilby layer, after the investigator who made extensive studies on the nature and properties of polish layers.

New Piston Rings - Treated Surfaces

In order to avoid extremely smooth surfaces on specimens subjected to electron-diffraction examination, the running faces of both new and used piston rings were roughened on a microscopic scale by abrading, etching, ruling, etc. In the case of new rings, the electron-diffraction patterns from the surfaces after (1) abrading with emery, (2) etching with 2 percent nital, (3) ruling with the diamond-point ruling machine, or (4) heating to 700° or 800° F in a vacuum, all showed a strong set of diffraction lines corresponding to the α-iron diffraction pattern, together with a few extra lines that corresponded to some of the stronger lines of Fe_3O_4. (The three strongest lines of the Fe_3O_4 pattern are given in table I as listed in the A.S.T.M. file of X-ray powder diffraction data, although this oxide cannot be distinguished from γ-Fe_2O_3 (reference 3.) Considerable variations occur in the sharpness of the lines and the intensity of the background, the best pattern being given by the ruled piston ring (fig. 3) and the poorest (although still recognizable) by the heated piston ring. Figure 4, for example, shows the results of abrading with emery paper in comparison with figure 3.

X-ray-diffraction patterns obtained by grazing incidence of the beam on the face of a new untreated piston ring showed mainly the α-iron pattern. Three extremely faint additional lines besides those of α-iron are as yet unidentified (table I).

The occurrence of the α-iron pattern as the chief feature of the various photographs from the new ring is understandable because the three largest minor constituents, nickel (3.5 percent), chromium (1.1 percent), and aluminum (1.3 percent), all form solid solutions in α-iron for the concentrations and thermal treatment used in the preparation of the steel before nitriding (references 4a, b, and c). In the nitriding process applied to piston rings, the reaction between nitrogen and iron produces a solid solution of nitrogen in α-iron or a mixture of the solid solution with the γ'-phase, Fe_4N, according to the concentration of nitrogen (reference 4d and fig. 5). The absence of any diffraction lines belonging to the γ'-phase indicates that the nitrogen concentration in the iron is very low, probably below 1 percent. The reaction between nitrogen and chromium or aluminum probably converts these elements completely to their nitrides but their low concentrations relative to the iron prevents their detection in a diffraction examination as reported by Hägg (reference 5). The α-iron pattern is to be expected from the piston-ring alloy because the dilute solid solutions of the minor constituents, including nitrogen, all have the α-iron structure with only slight changes in the lattice dimensions.

Used Rings - Treated Surfaces

The segments of used rings were taken from two different engine tests. Those segments that were etched showed varying degrees of surface coverage by the coating, as described in reference 1. The electron-diffraction photographs of the used rings after etching (fig. 6), abrading, or in one case, after ruling, as well as the X-ray photographs of the used ring, often showed the α-iron pattern as their principal feature. This appearance of the same pattern from new and used rings raised the question of whether the pattern from the used ring is characteristic of the wear coating or of the uncoated metal. The surface disturbance produced by the acid etch occurred mainly on the basis metal since the coating has been previously shown (reference 1) to be relatively acid-resistant and the uncoated surface was accordingly in a more favorable state for electron diffraction. In the abrasion with emery, the two parts of the surface acted differently because of the greater hardness of the coating, as shown by the narrower scratches produced on the coated areas in Bierbaum microhardness tests. Previous measurements (reference 1) were made on two specimens, one fairly uniformly coated and one uncoated. Both were lightly polished before examination.

The coating under these conditions was found to be softer than the basis metal. The hardness measurements investigated herein on a number of specimens, which were not polished or rubbed in any way, have shown coating material to be harder than the basis metal. A single continuous scratch was used in the latter measurements to determine hardnesses as it crossed both coated and uncoated areas on each specimen. Under light abrasion the uncoated surface will be roughened more, whereas under heavy abrasion the thin coating is likely to be removed entirely, as demonstrated by etching subsequent to heavy abrasion. It is probable that the α-iron pattern from the used ring was due to the basis metal and not to the coating.

A notable feature of the X-ray photographs is that the three lines occurring in addition to the α-iron pattern fall at positions corresponding to the (200), (220), and (311) lattice planes of γ-iron. The lines corresponding to the other planes of γ-iron, (111), (222), (400), and (331, 420), which complete the pattern within the range observed, coincide with certain lines of the α-iron pattern. The first eight lines of the γ-iron pattern are therefore accounted for. The relative intensities of the lines not common to both patterns indicated that a considerable fraction of the iron had the γ-structure although the greater part had the α-structure. This conclusion is supported by the electron-diffraction photographs of etched and abraded rings, although the number of extra rings in the pattern is smaller and their relative intensity is less. In both the electron and X-ray-diffraction experiments, the evidence for γ-iron appeared from the used rings but not from the new rings.

The γ-iron in the used ring had probably been produced by high-surface temperatures and pressures but it did not lie in the outermost surface layer, as shown by the weakness of the lines in the electron-diffraction pattern and their greater relative intensity in the pattern obtained by X-rays, which penetrated more deeply than the electrons. The γ-iron is perhaps to be associated with the disturbed region below the surface shown in metallographic taper sections given in reference 1 but it is probably not characteristic of the coating.

The formation of layers of α- and γ-iron produced by grinding has been noted in reference 6. In the case cited, the bulk material was predominately austenite. During grinding a layer of ferrite was formed intermediately between an upper layer of austenite and the bulk material. It seems likely that a stratified structure exists in the material at the surface of the piston rings studied in this investigation.

Some evidence concerning the nature of the coating was afforded by electron-diffraction observations on segments taken from the same used ring. Two segments were ruled in the diamond-point machine, designed to give scratches of controlled depth over particular areas, and one showed the α-iron pattern more sharply defined than in the photographs made from used rings scratched with emery. The other segment gave two diffuse lines occurring at spacings already identified as those formed for polish layers. A number of faint diffuse lines in the pattern, in addition to the two principal lines, have not yet been observed distinctly enough for precise measurements. They definitely do not have the spacings belonging to α- or γ-iron, which indicates the presence of a material differing from the basis metal of the piston ring. The lines do not agree with any previously known patterns of compounds of the elments in the alloy or with any of the oxides of iron.

A difference between the surfaces of new and used rings was also found in experiments on heating the piston rings to 700° or 800° F in a vacuum. The new ring gave the α-iron electron-diffraction pattern after heating although not so sharp as after abrasion. The used rings after heating gave only two diffuse lines that did not arise from α- or γ-iron and cannot definitely be distinguished from the similar pattern mentioned in the preceding paragraph.

SUMMARY OF RESULTS

The results of the electron and X-ray-diffraction studies of the surface changes produced on the faces of nitrided-steel piston rings by engine operation can be summarized as follows:

1. Both the new and used rings treated only for removal of any oil film gave two diffuse bands in electron diffraction. These bands are not useful in the identification of the coating under investigation but it was noted that the bands from the used ring correspond to the pattern previously observed from polished metal surfaces.

2. The new rings after microscopic roughening of the faces gave the electron-diffraction pattern of α-iron or its dilute solid solutions with the minor constituents of the alloy, including nitrogen, together with a weaker pattern of Fe_3O_4 or γ-Fe_2O_3. X-ray diffraction by reflection of the rays from the ring face showed the α-iron pattern.

3. Used rings after roughening usually showed, by electron diffraction, α-iron and Fe_3O_4 or γ-Fe_2O_3, as well as traces of γ-iron. X-ray beams penetrating more deeply (0.005 in.) showed α-iron and larger relative amounts of γ-iron.

4. Evidence for the coating has been clearly observed in the pattern from a segment of a used ring roughened by ruling in a diamond-point machine. Because of the discontinuous character of the coating, one segment under this treatment showed only α-iron, the basis metal; whereas, an adjacent one showed the two bands observed from the unruled ring in addition to several sharper lines, which have not been identified, but are not due to α-iron, γ-iron, or any of the oxides of iron and do not belong to patterns of compounds of the constituents of the alloy.

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TABLE I

OBSERVED LATTICE SPACINGS FROM DIFFRACTION PATTERNS OF NITRIDED-STEEL PISTON RINGS AND COMPARISON STANDARDS

[d, interplanar spacings in angstrom units A; I, intensities graded: S - strong, M - medium, F - faint, V - very]

New ring				Used ring				Standard patterns								
Electron diffraction (specimen emery abraded)		X-ray diffraction (untreated specimen)		Electron diffraction (specimen emery abraded)		X-ray diffraction (untreated specimen)		α-Fe			γ-Fe			[a]Fe_3O_4		
d(A)	I	[b]d(A)	I	d(A)	I	d(A)	I	d(A)	I/I_1	Miller indeces (hkl)	d(A)	I/I_1	Miller indeces (hkl)	d(A)	[c]I/I_1	Miller indeces (hkl)
2.53 [d]±0.04	S	---- -----	---	2.49 [d]±0.04	S	---- -----	---	-----	----	----	----	----	----	2.53	1.0	311
2.01 .03	VS	2.06 [e]0.13	VVS	2.02 .03	VS	2.03 [e]0.13	VS	2.02	1.0	110	2.05	0.9	111	----	-----	----
---- ------	---	---- -----	---	1.75 .02	F	1.79 .08	M	-----	----	----	1.78	.6	200	----	-----	----
1.69 .02	VF	---- -----	---	---- ------	--	---- -----	---	-----	----	----	----	----	----	----	-----	----
1.61 .02	VF	---- -----	---	1.61 .02	VF	---- -----	---	-----	----	----	----	----	----	1.61	.6	511,333
1.46 .01	M	1.44 .08	M	1.45 .01	M	1.43 .01	M	1.43	.5	200	----	----	----	1.48	.8	440
1.31 .01	VF	---- -----	---	---- ------	--	---- -----	---	-----	----	----	----	----	----	----	----	----
---- ------	---	---- -----	---	1.28 .02	VF	1.23 .08	F	-----	----	----	1.26	.7	220	----	----	----
1.16 .01	S	1.17 .06	S	1.16 .01	M	1.15 .03	M	1.17	.8	211	----	----	----	----	----	----
---- ------	---	---- -----	---	---- ------	--	1.07 .03	VF	-----	----	----	1.07	1.0	311	----	----	----
1.04 .01	VF	1.01 .05	VF	---- ------	--	.99 .04	VF	1.01	.5	220	1.03	.3	222	----	----	----
.92 .01	F	.90 .04	F	---- ------	--	.88 .02	VF	.91	.6	310	.89	.2	400	----	----	----
.85 ------	VF	---- -----	---	---- ------	--	.81 .03	VVF	.83	.2	222	.82	.6	331	----	----	----
.80 ------	VF	---- -----	---	---- ------	--	---- -----	---	-----	----	----	.80	.6	420	----	----	----
.76 ------	F	.76 .03	F	---- ------	--	.75 .01	VVF	.76	.6	321	.73	.5	422	----	----	----
.68 ------	VVF	.67 .03	VVF	---- ------	--	---- -----	---	.68	.3	411,330	.68	.2	511,333	----	----	----

[a]The d and I/I_1 values were obtained from A.S.T.M. X-ray diffraction data card 2834.

[b]Three very weak and unidentified lines also found in this pattern are: 2.66, 1.90, and 1.72 A.

[c]The lines given here are the three strongest lines in the pattern, $I/I_1 \geq 0.5$.

[d]The ± uncertainty in d values due to ±0.1 minimum uncertainty in the measurement of electron-diffraction photographs

[e]The width of X-ray diffraction line due to length of specimen.

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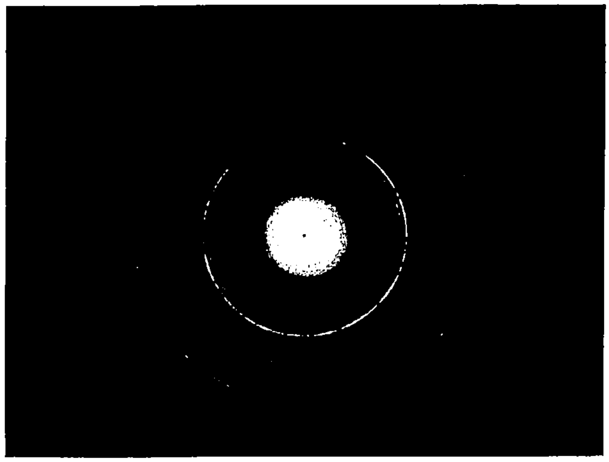

Figure 1.—Standard transmission pattern obtained from zinc oxide used for calibration. $\times 3$.

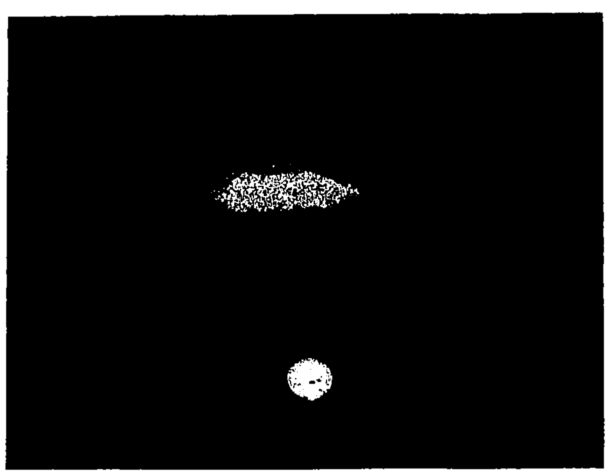

Figure 2.—Electron-diffraction pattern from the surface of a new nitrided-steel piston ring. These diffuse bands are characteristic of the untreated surface. $\times 3$.

Figure 3.—Electron-diffraction pattern from the surface of a new nitrided-steel piston ring. This pattern of α-iron was obtained after the surface had been microscopically ruled with 8,000 parallel lines to the inch. ×3.

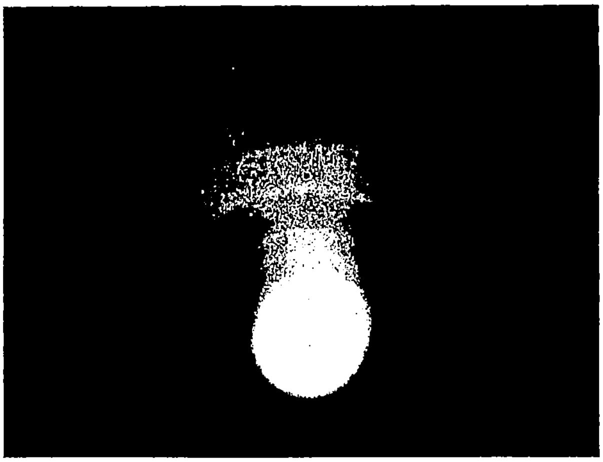

Figure 4.—Electron-diffraction pattern from the surface of a new nitrided-steel piston ring after abrasion with emery. The pattern is that of α-iron except for the innermost ring, which is the strongest belonging to the pattern of either Fe_3O_4 or γ-Fe_2O_3. ×3.

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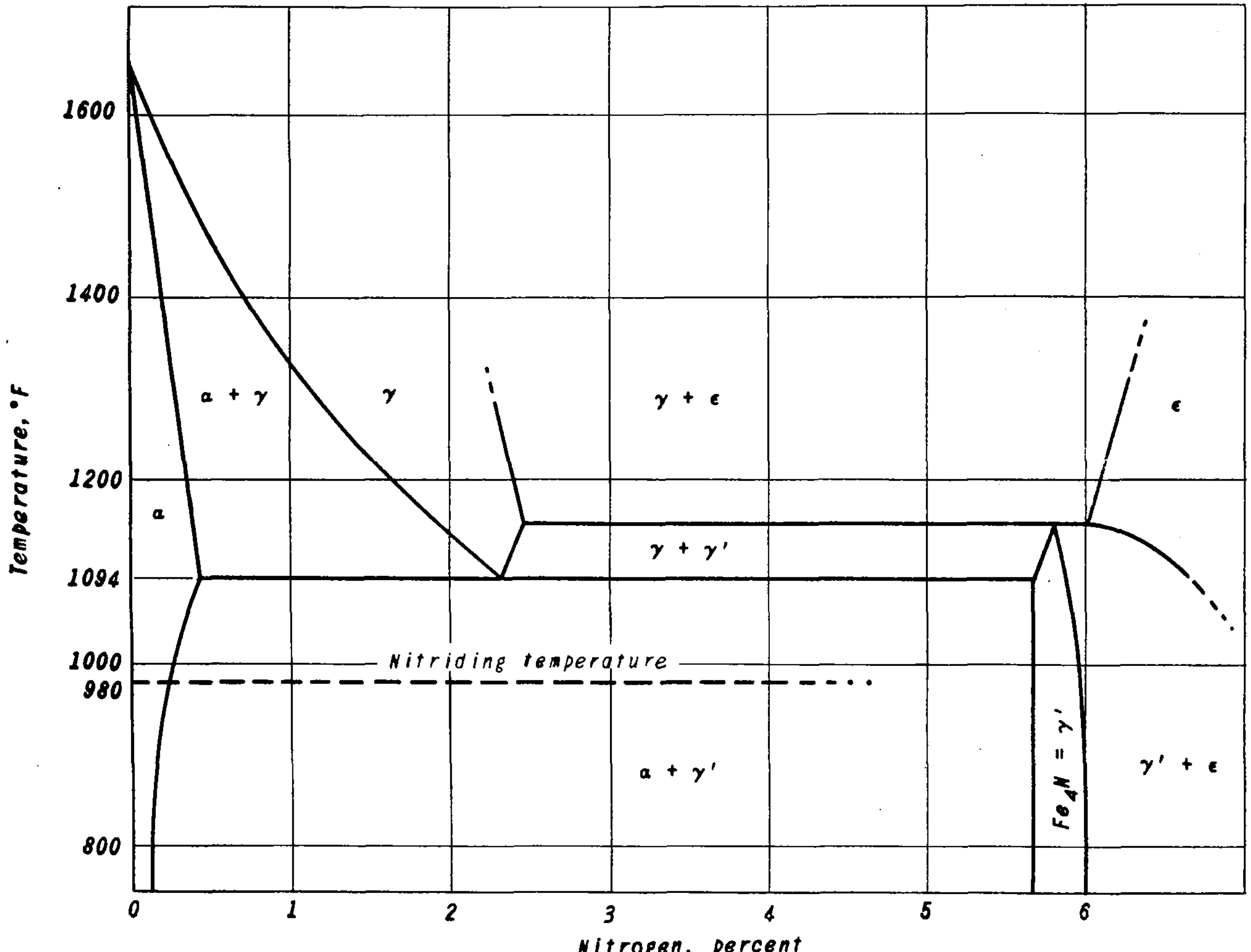

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Figure 5. - Iron-nitrogen system. The line at 980° F indicates the phase equilibriums at the nitriding temperature. (Taken from reference 4d, fig. 4.)

Figure 6.—Electron-diffraction pattern from the etched surface of a used nitrided-steel piston ring. This pattern of α-iron was obtained from the basis metal because of the irregular coverage of the ring faces by coating. $\times 3$.

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